

FORM PTO-1590
(REV. 11-2000)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371**

Mo-6204/LeA 33,181

U.S. APPLICATION NO. (if known, see 37 CFR 1.5

09/762800
To Be Assigned

INTERNATIONAL APPLICATION NO.

INTERNATIONAL FILING DATE

PCT/EP99/05640

August 4, 1999

PRIORITY DATE CLAIMED

August 17, 1998

TITLE OF INVENTION MEDIA FOR WATER TREATMENT

APPLICANT(S) FOR DO/EO/US KLEINSTUCK, Roland; GROTH, Torsten and JOENTGEN, Winfried

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☒ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☐ is attached hereto.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11 to 20 below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
14. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information:

Abstract

U.S. APPLICATION NO. **08/762800**
To Be AssignedINTERNATIONAL APPLICATION NO.
PCT/EP99/05640ATTORNEY'S DOCKET NUMBER
Mo-6204/LeA 33,18121. ☒ The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):

Neither international preliminary examination fee (37 CFR 1.482)
nor international search fee (37 CFR 1.445(a) (2)) paid to USPTO
and International Search Report not prepared by the EPO or JPO \$100.00International preliminary examination fee (37 CFR 1.482) not paid to
USPTO but International Search Report prepared by the EPO or JPO \$860.00International preliminary examination fee (37 CFR 1.482) not paid to USPTO
but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$710.00International preliminary examination fee (37 CFR 1.482) paid to USPTO
but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$690.00International preliminary examination fee (37 CFR 1.482) paid to USPTO
and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00**ENTER APPROPRIATE BASIC FEE AMOUNT =**Surcharge of \$130.00 for furnishing the oath or declaration later than ☐ 20 ☐ 30
months from the earliest claimed priority date (37 CFR 1.492(e)).

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total claims	11 -20 =	0	x \$18.00	\$ 0.00
Independent claims	2 -3 =	0	x \$80.00	\$ 0.00
			+ \$270.00	\$ 0.00

MULTIPLE DEPENDENT CLAIM(S) (if applicable)

TOTAL OF ABOVE CALCULATIONS =☒ Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above
are reduced by 1/2.**SUBTOTAL =**Processing fee of \$130.00 for furnishing the English translation later than ☐ 20 ☐ 30
months from the earliest claimed priority date (37 CFR 1.492(f)).**TOTAL NATIONAL FEE =**Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be
accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +**TOTAL FEES ENCLOSED =**

CALCULATIONS PTO USE ONLY

\$ 860.00

\$ 0.00

\$ 0.00

\$ 0.00

\$ 0.00

\$ 860.00

\$ 0.00

\$ 860.00

\$ 0.00

\$ 860.00

\$ 40.00

\$ 900.00

Amount to be
refunded: \$

charged: \$

- a. ☐ A check in the amount of \$ _____ to cover the above fees is enclosed.
- b. ☒ Please charge my Deposit Account No. 13-3848 in the amount of \$ 900.00 to cover the above fees.
A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any
overpayment to Deposit Account No. 13-3848. A duplicate copy of this sheet is enclosed.
- d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card
information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR
1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

Diderico van Eyl
Bayer Corporation
Patent Department
100 Bayer Road
Pittsburgh, PA 15205-9741**00157**
PATENT TRADEMARK OFFICE

SIGNATURE

Diderico van Eyl
NAME38,641

REGISTRATION NUMBER

TRANSMITTAL LETTER TO THE
UNITED STATES RECEIVING OFFICE

Date	February 13, 2001
International Application No.	PCT/EP99/05640
Attorney Docket No.	Mo-6204/LeA 33,181

I. Certification under 37 CFR 1.10 (if applicable)

EL062670601US
Express Mail mailing number

February 13, 2001
Date of Deposit

I hereby certify that the application/correspondence attached hereto is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to Assistant Commissioner for Patents, Washington, D.C. 20231.

Signature of person mailing correspondence

Donna J. Veatch
Typed or printed name of person mailing correspondence

II. ☒ New International Application

TITLE	MEDIA FOR WATER TREATMENT
-------	---------------------------

Earliest priority date (Day/Mon/Year)
(17/08/98)

SCREENING DISCLOSURE INFORMATION: In order to assist in screening the accompanying international application for purposes of determining whether a license for foreign transmittal should and could be granted and for other purposes, the following information is supplied. (Note: check as many boxes as apply):

- A. ☒ The invention disclosed was not made in the United States.
- B. ☒ There is no prior U.S. application relating to this invention.
- C. ☐ The following prior U.S. application(s) contain subject matter which is related to the invention disclosed in the attached international application. (NOTE: priority to these applications may or may not be claimed on form PCT/RO/101 (Request) and this listing does not constitute a claim for priority.)

application no.	filed on
application no.	filed on

- D. ☐ The present international application ☐ contains additional subject matter not found in the prior U.S. application(s) identified in paragraph C. above. The additional subject matter is found on pages and ☐ DOES NOT ALTER ☐ MIGHT BE CONSIDERED TO ALTER the general nature of the invention in a manner which would require the U.S. application to have been made available for inspection by the appropriate defense agencies under 35 U.S.C. 181 and 37 CFR 5.1. See 37 CFR 5.15

III. ☐ A Response to an Invitation from the RO/US. The following document(s) is(are) enclosed:

- A. ☐ A Request for An Extension of Time to File a Response
- B. ☐ A Power of Attorney (General or Regular)
- C. ☐ Replacement pages:

pages	of the request (PCT/RO/101)	pages	of the figures
pages	of the description	pages	of the abstract
pages	of the claims		

- D. ☐ Submission of Priority Documents

Priority document	Priority document
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- E. ☐ Fees as specified on attached Fee Calculation sheet form PCT/RO/101 annex

IV. ☐ A Request for Rectification under PCT 91 ☐ A Petition ☐ A Sequence Listing Diskette

- V. ☒ Other (please specify): Preliminary Amendment w/Abstract

The person
signing this
form is the:

<input type="checkbox"/> Applicant	Diderico van Eyl	
<input checked="" type="checkbox"/> Attorney/Agent (Reg. No.) 38,641		
<input type="checkbox"/> Common Representative		Signature

09/762800

JC02 Rec'd PCT/PTO 13 FEB 2001

PATENT APPLICATION
Mo-6204
LeA 33,181

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICATION OF)
) PCT/EP99/05640
ROLAND KLEINSTÜCK ET AL)
)
SERIAL NUMBER: TO BE ASSIGNED)
)
FILED: HEREWITH)
)
TITLE: MEDIA FOR WATER TREATMENT)

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents

Washington, D.C. 20231

Sir:

Prior to examination of the subject application, please amend as follows:

IN THE CLAIMS:

1. (Amended) A composition [Composition] for water treatment comprising
 - a) biodegradable organic polymers having repeating succinyl units
 - b) a biocidal oxidizing agent
 - c) an unsubstituted or substituted amidosulphonic acid.
2. (Amended) The composition of [Composition for water treatment according to] Claim 1, [characterized in that] wherein the amidosulphonic acid comprises [of the formula]



[is used].

"Express Mail" mailing label number EL062670601US
Date of Deposit February 13, 2001

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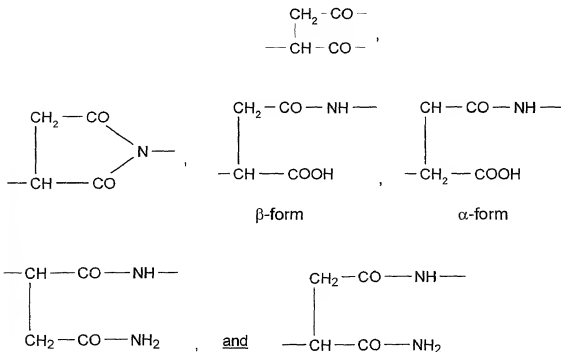
Donna J. Veatch

(Name of person making paper or fee)



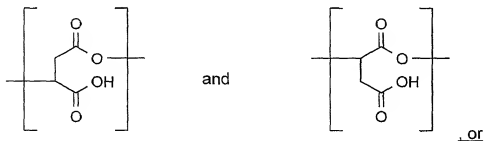
Signature of person mailing paper or fee)

3. (Amended) The composition according to Claim 1, wherein
 [Composition for water treatment according to Claims 1 and 2, characterized in that]
 the biodegradable organic polymers have repeating succinyl units of the structures
selected from the group consisting of

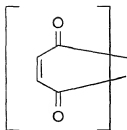


4. (Amended) The composition according to Claim 1, wherein
 [Composition for water treatment according to Claims 1 to 3, characterized in that]
 the biodegradable organic polymers contain repeating units of the formulae

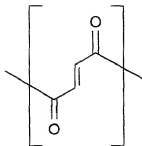
a) maleic acid units of the formula



b) maleic acid and fumaric acid units of the formula



and



5. (Amended) The composition according to Claim 1, wherein

[Composition for water treatment according to Claims 1 to 4, characterized in that] the biocidal oxidizing agent is hydrogen peroxide, chlorine, bromine, chlorine dioxide, hypochlorite, hypobromite, or ozone [or their reaction products] or a reaction product of (i) a component selected from the group consisting of hydrogen peroxide, chlorine, bromine, chlorine dioxide, hypochlorite, hypobromite, and ozone [with] and (ii) water.

Please cancel Claims 6-7:

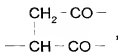
Please add new Claims 8-13:

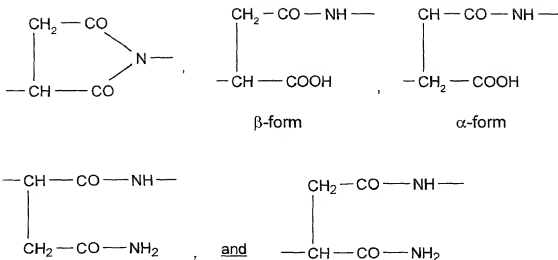
-8. A process for treating water comprising introducing to a water component a composition containing (a) biodegradable organic polymers having repeating succinyl units, (b) a biocidal oxidizing agent, and (c) an unsubstituted or substituted amidosulphonic acid.

9. The process according to Claim 8, wherein the water is water of a cooling circuit.

10. The process according to Claim 8, wherein the amidosulphonic acid comprises $\text{H}_2\text{NSO}_3\text{H}$.

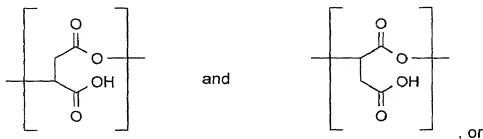
11. The process according to Claim 8, wherein the biodegradable organic polymers have repeating succinyl units of the structures selected from the group consisting of:



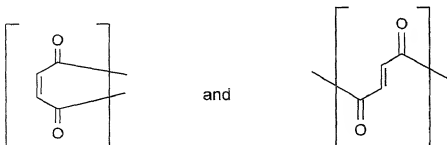


12. The process according to Claim 8, wherein the biodegradable organic polymers contain repeating units selected from the group consisting of units having the formulae

(a) maleic acid units of the formula



(b) maleic acid and fumaric acid units of the formula



13. The process according to Claim 8, wherein the biocidal oxidizing agent is hydrogen peroxide, chlorine, bromine, chlorine dioxide, hypochlorite,

hypobromite, or ozone; or a reaction product of (i) a component selected from the group consisting of hydrogen peroxide, chlorine, bromine, chlorine dioxide, hypochlorite, hypobromite, and ozone and (ii) water.--

IN THE SPECIFICATION

Please amend the specification as follows:

In the Title, please cancel the Title and replace with the following Title:

--MEDIA FOR WATER TREATMENT--

On page 1, below the Title, please add:

--BACKGROUND--

On page 3, below line 2, please add:

--DESCRIPTION--

At page 10, below line 8, please add:

--The invention is further described in the following illustrative examples in which all parts and percentages are by weight unless otherwise indicated.--

At page 13, below the table, please add:

--Although the present invention has been described in detail with reference to certain preferred versions thereof, other variations are possible. Therefore, the spirit and scope of the appended claims should not be limited to the description of the versions contained therein.--

Please add the following Abstract, submitted herein separately:

--MEDIA FOR WATER TREATMENT

ABSTRACT OF THE DISCLOSURE

The present invention relates to compositions for water treatment based on biodegradable polymers containing repeating succinyl units, biocidal oxidizing agents and unsubstituted or substituted amidosulphonic acid, their use in, and the process for, conditioning water of cooling circuits.--

REMARKS

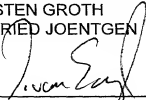
Entry of this Preliminary Amendment is requested. The amendments made above were made to place the Application in conformance with U.S. practice. No new matter was added. Claims 6-7 were cancelled. Claims 8-13 were added. Support for Claims 8-9 can be found on page 9, lines 25-27 of the specification and the examples. Support for Claim 10 can be found at page 3, lines 26-30. Support for Claim 11 can be found at page 4, lines 1-10. Support for Claim 12 can be found at page 4, lines 10-26. Support for Claim 13 can be found at page 6, line 26 to page 7, line 2.

In view of the amendments above, entry of this Preliminary Amendment is requested.

Respectfully submitted,

ROLAND KLEINSTÜCK
TORSTEN GROTH
WINFRIED JOENTGEN

By


Diderico van Eyll
Attorney for Applicants
Reg. No. 38,641

Bayer Corporation
100 Bayer Road
Pittsburgh, Pennsylvania 15205-9741
(412) 777-4802
FACSIMILE PHONE NUMBER:
(412) 777-5449
s:/sr/dv0295

MEDIA FOR WATER TREATMENT
ABSTRACT OF THE DISCLOSURE

The present invention relates to compositions for water treatment based on biodegradable polymers containing repeating succinyl units, biocidal oxidizing agents and unsubstituted or substituted amidosulphonic acid, their use in, and the process for, conditioning water of cooling circuits.

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Donna J. Veatch
(Name of person mailing paper or fee)
Donna J. Veatch
Signature of person mailing paper or fee

09762800

Compositions for water treatment

5 The present invention relates to compositions for water treatment based on biodegradable polymers containing repeating succinyl units, biocidal oxidizing agents and a substituted or unsubstituted amidosulphonic acid, their use in, and the process for, conditioning water of cooling circuits.

10 When natural waters are used for industrial purposes, for example as cooling water, the water used is changed physically and/or possibly also chemically specifically or unintentionally. Thus, for example, in open recirculating cooling systems, temperature changes, concentration and a pH increase due to the discharge of carbon dioxide in the cooling tower are unavoidable.

15 Due to the concentration and increase in pH from the discharge of CO₂, the concentration of hardness constituents, in particular calcium ions and carbonate ions, increases. If the natural waters were in equilibrium before use (lime-carbon dioxide equilibrium), an increase in concentration of the hardness constituents leads to supersaturation. To prevent scale deposition (encrustations), in particular on heat-transfer surfaces, treatment of the waters by addition of additives ("scale inhibitors")
20 is necessary.

A further, sometimes even the predominant, purpose of the use of additives in water treatment is protection of metallic materials against corrosion. For example, when
25 unalloyed carbon steels are used in open recirculating cooling systems, adequate corrosion inhibition is desired, since the conditions prevailing in such systems (oxygen saturation, salt accumulation) lead to an acceleration of corrosion.

WO 97/39078 proposes the use of biodegradable polymers, such as, for example,
30 polyaspartic acid, or other aspartic-acid-containing polymers in combination with biocidally acting oxidizing agents to condition water in cooling circuits.

Descriptions are given, inter alia, of experiments in which 10 mg/l of polyaspartic acid having a molecular weight of about 3000 were tested in the presence of 0.4 mg/l of sodium hypochlorite for scale-inhibiting activity, and no decrease in scale-inhibiting activity was observed over the measurement period of 4 hours. When
5 0.4 mg/l of a mixture of sodium hypochlorite and sodium hypobromite in a weight ratio of 1:1 was added, 95% of the initial activity was still present after 4 hours.

Furthermore, in a cooling circuit having a cooling tower, the concentration of polyaspartic acid was tested without and with addition of 0.2 mg/l of chlorine in the
10 form of sodium hypochlorite over one month: without chlorine addition, with daily doses of 20 to 50 mg/l of polyaspartic acid, a concentration of between 11 mg/l and 2 mg/l was established, and with chlorine addition a concentration of about 20 mg/l was established.

A disadvantage of the mixtures of WO 97/39078 is the fact that the polymers used there react to a considerable extent with microbicides such as chlorine, bromine or
15 halogen-releasing products, which is observable by a decrease in the biocide concentration.

It must be expected that owing to the reaction with the biocide, portions of polyaspartic acid are also destroyed, and that, as a result, the desired scale-inhibiting
20 and/or corrosion-inhibiting activity is no longer achieved.

In many cases, although it would be possible to create a compensation at least to a certain extent by a higher dosage of the polyaspartic acid, the economic efficiency of
25 the use of polyaspartic acid would suffer.

Therefore, the object of the present invention is to provide a composition for water treatment based on polymers containing repeating succinyl units, the components of
30 which polymers remain stable over a long period, so that the use is economically

justifiable, even in cooling circuits, especially in those having relatively long residence times.

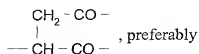
5 The object was achieved by means of the fact that polymers containing repeating succinyl units are mixed with biocidally acting oxidizing agents and, as stabilizer, unsubstituted or substituted amidosulphonic acid is added. The stabilizer here has the task of preventing or substantially reducing the reaction between polymer and oxidizing agent.

10 Although the use of ammonia, amines, amides or amidosulphonic acids as stabilizers for chlorine is disclosed by US-P 4,711,724 and US-P 3,170,883, and US-P 4,642,194 describes the use of amidosulphonic acids and organic sulphonamides (EP-A 0 569 220) as stabilizers for specific phosphonic acids with respect to chlorine and US-P 4,759,852 also with respect to bromine, the use of
15 amidosulphonic acid and organic derivatives of amidosulphonic acid for stabilizing polyaspartic acid with respect to chlorine and bromine, has not previously been mentioned in the literature.

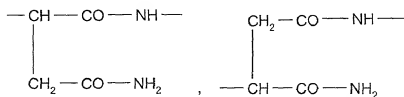
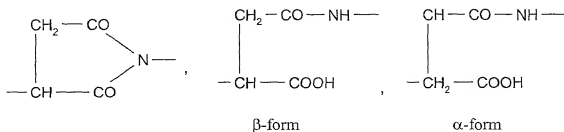
20 The high efficacy of amidosulphonic acid for stabilizing halogen with respect to polymers containing repeating succinyl units is surprising to those skilled in the art, since amide structures are present in the polymers themselves. The addition of a further amide should therefore give rise to the expectation of little activity. Surprisingly, by this means, the reaction between oxidizing biocide and polymer was considerably reduced.

25 The present invention therefore relates to the use of polymers containing repeating succinyl units, in particular polyaspartic acids, as compositions for water treatment in combination with a biocide and amidosulphonic acid H_2NSO_3H or organic derivatives of amidosulphonic acid, and to the use of these compositions for water
30 conditioning of cooling circuits.

The polymers used according to the invention have repeating succinyl units having one of the following structures:



5

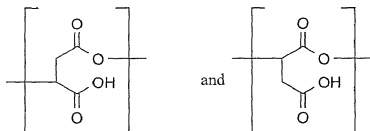


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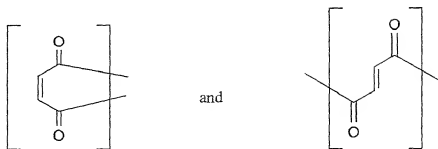
In addition, as a result of suitable reaction procedure and choice of starting materials, further repeating units can be present, e.g.

a) maleic acid units of the formula

15



b) maleic acid and fumaric acid units of the formula



The chemical structure is preferably analysed by ^{13}C -NMR, FT-IR and, after total hydrolysis, by HPLC, GC and GC/MS.

5

Many preparation processes produce not the pure acids, but initially the corresponding anhydrides, for example polysuccinimide (= PSI). Polymerization products of this type can be converted into a salt of PAA by reaction with a base in the presence or absence of water. This conversion of PSI polymers to PAA polymers takes place subsequently in a suitable apparatus by hydrolysis. Preference is given here to a pH between 5 and 14. Particularly preferably, a pH of 7 to 12 is selected, in particular by adding a base. Suitable bases are alkali metal hydroxides and alkaline earth metal hydroxides or alkali metal carbonates and alkaline earth metal carbonates, such as sodium hydroxide solution, potassium hydroxide solution, soda or potassium carbonate, ammonia and amines such as triethylamine, triethanolamine, diethylamine, diethanolamine, alkylamines etc. Particular preference is given, in addition to the free acids, to their Na, K or Ca salts.

10

15

20

The temperature during the hydrolysis is suitably in a range up to and including the boiling point of the PSI suspension and is preferably 20 to 150°C. The hydrolysis is carried out under pressure, if appropriate.

25

However, it is also possible to obtain the free polyaspartic acid by purely aqueous hydrolysis or treating the salt with acids or acidic ion-exchangers. The term "polyaspartic acid" (= PAA) for the purposes of the present invention likewise includes the salts, unless explicitly stated otherwise.

The final polyaspartic acid or the salts of polyaspartic acid are obtained by drying, preferably spray-drying.

5 Preferred polymers have a molecular weight, according to gel-permeation chromatography, of $MW = 500$ to $10,000$, preferably 700 to 5000 , particularly preferably 1000 to 4500 . Generally, the beta-form content is more than 50% , preferably more than 70% .

10 The concentration of the polyaspartic acids to be used for the water treatment is usually approximately 0.5 to 100 mg/l of active compound in the aqueous phase, but mostly in the range from approximately 2 to 50 mg/l.

15 To achieve the object of the present invention, in addition, biocides are used. Preferably, use is made of biocidal oxidizing agents having a standard redox potential more positive than oxygen.

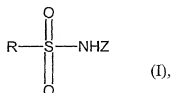
20 Standard redox potentials, also termed standard potentials, are generally known thermodynamic terms, which are described in textbooks of general or physical chemistry. An example which may be mentioned is chapter 11 of the textbook: H.R. Christen "Grundlagen der allgemeinen und anorganischen Chemie" [Principles of General and Inorganic Chemistry], Verlag Sauerländer-Salle, 1973. This textbook, on pages 692 to 697, contains a list of different standard potentials, which can also be found in many other textbooks and tabulations. The magnitude of the standard redox potential is usually expressed in volts.

25 Preferably, for the application according to the invention, oxidizing agents having a standard redox potential greater than 0.4 volts are used. Preferably, the oxidizing agent selected is hydrogen peroxide, chlorine, bromine, chlorine dioxide, hypochlorites, hypobromites or ozone. Since these chemicals in the presence of water
30 can participate in acid-base reactions and/or disproportionation reactions, the

abovementioned oxidizing agents are also taken to mean their reaction products with water.

The biocides are used in the compositions according to the invention for water treatment in concentrations of 0.05 to 20 mg/l. Preferably 0.05 to 10 mg/l, especially preferably 0.1 to 5 mg/l, of biocide are used.

As stabilizers of the biocides, use is made of unsubstituted or substituted amidosulphonic acids of the formula (I)



where

Z represents hydrogen, lithium, sodium, potassium, magnesium or calcium and

R represents an unsubstituted or substituted radical from the group consisting of OH, C₁-C₄-alkyl, C₁-C₄-alkoxy, amino, mono(C₁-C₄-alkyl)amino, di(C₁-C₄-alkyl)amino, formylamino, -NHC(O)C₁-C₄-alkyl, -NHC(O)OC₁-C₄-alkyl, C₂-C₆-alkenyl, C₂-C₆-alkinyl, C₃-C₇-cycloalkyl, unsubstituted or substituted phenyl, naphthyl, pyridyl, pyrimidyl, pyrazyl, pyridazyl, pyrrolyl, imidazolyl, pyrazolyl, triazolyl, tetrazolyl, suitable substituents in each case being: C₁-C₄-alkyl, C₁-C₄-alkoxy, C₁-C₄alkoxycarbonyl, halogen, nitro, nitrilo, carboxyl, -S(O)_nC₁-C₄-alkyl where n = 2 and each of which is optionally substituted on the nitrogen by one or two C₁-C₄-alkyl groups, sulfamoyl, -SO₂N(R¹)R² where R¹ and R² each denote C₁-C₄-alkyl.

Preferably, use is made of an unsubstituted or substituted amidosulphonic acid of the formula (I) where $R = OH$, $-C_6H_4-CH_3$ (tolyl) and OCH_3 and Z represents hydrogen, sodium and potassium.

- 5 In particular, preference is given to the amidosulphonic acid of the formula (I) where R represents OH and Z represents hydrogen.

The stabilizers are used in amounts of 0.02 to 15 mg/l. Preferably, 0.1 to 10 mg of stabilizer, in particular 0.2 to 5 mg of stabilizer, per l are used.

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It is customary, and to be preferred for the purposes of the invention, that the water phase of the aqueous cooling system additionally comprises other components which can have an inhibitory action on corrosion or scale or a dispersive action. Those which may be mentioned by way of example are: 1 to 10 mg/l of zinc ions, 1 to 200 mg/l of monomeric or oligomeric molybdate ions, organic phosphates in a concentration such that the phosphorus content, calculated as phosphate, is in the range 1 to 20 mg/l of phosphate, monomeric, oligomeric or polymeric inorganic phosphates at a concentration such that the phosphorus content, calculated as phosphate, is in the range 1 to 20 mg/l of phosphate, and nonferrous metal inhibitors, such as triazoles. As further anticorrosion components, the water phase can comprise known active compounds, such as alkanolamines, in particular triethanolamine, borates, sorbitol, nitrites, nitrates and silicates. As further additives having corrosion-inhibiting and/or dispersive action, use can be made of: phosphate esters, polyphosphoric esters, aminophosphates, aminomethylenephosphonic acids, phosphonates, in particular hydroxyalkanediphosphonic acids, hydroxyphosphonoacetic acid, aminoalkylenephosphonic acids, phosphonocarboxylic acids, succinamide, gluconates, polyoxycarboxylic acids and their copolymers, tannin derivatives, lignosulphates, sulphonated condensation products of naphthalene with formaldehyde, polyacrylates, polymethacrylates, polyacrylamides, polymaleates, copolymers of acrylic acid or methacrylic acid, maleic acid and acrylamide, phosphinic-acid-containing homopolymers and copolymers of acrylic acid and

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acrylamide, oligomeric phosphinosuccinic acid compounds, sulphomethylated or sulphoethylated polyacrylamides and copolymers or terpolymers with acrylic acid, maleic acid, N-butylacrylamide, acrylamidopropionosulphonic acid, maleic anhydride polymers and copolymers, phosphinoalkylated acrylamide polymers and copolymers with acrylic acid, citric acid, ethercarboxylates or oxidized carbohydrates.

To achieve an optimum corrosion protection, the water phase of the aqueous cooling systems is preferably adjusted to a pH in the range of about 7 to about 9. The biocidal oxidizing agents can be metered into the cooling system continuously or preferably batchwise in the form of an intermittent treatment.

The aqueous cooling systems can be through-flow systems or open or closed circulation systems. The invention is designed particularly for use in open circuit systems, since it is especially suitable for counteracting the problems which occur in such systems of scale formation, the formation of deposits and/or biological contamination.

The compositions according to the invention can be used in a versatile manner, for example as scale inhibitors and also corrosion inhibitors and biocides. Fields of use of such compositions can be, for example: water treatment (e.g. treatment of cooling waters, process waters, gas scrubbing waters, injection waters in secondary oil extraction and water treatment in mining).

The present invention further relates to a process for water treatment which is characterized in that the composition according to the invention is introduced into the water to be treated.

The water treatment process is to be illustrated with reference to examples below:

For example, the compositions according to the invention are added to the feed water at concentrations between about 0.1 and 10 mg/l of active compound to prevent depositions and scales when used in cooling systems using fresh water cooling.

- 5 In cooling circuits, the additives are frequently metered rate-independently to the make-up water, for scale prevention and/or corrosion prevention. The concentrations are between about 1 and 100 mg/l of active compound in the circulating cooling water.

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Example 1

In a clear glass flask, 1 l of cooling water having a total hardness of 3.0 mmol/l ($\hat{=}$ 17° dGH [German degrees of total hardness]), of which 80 mol% is carbonate hardness, and $K_{S\ 4,3} = 3.2$ mmol/l ($\hat{=}$ 9° dKH [German degrees of carbonate hardness]) was admixed with 10 mg/l of sodium polyaspartate and 5 ml of a dilute bleaching liquor solution containing 1000 mg/l as chlorine. The pH was adjusted to 7.0 using hydrochloric acid, the flask was sealed and stored at room temperature for 24 h.

Similar samples were prepared having the following variants:

- pH set to 8.5 by addition of sodium hydroxide solution,
- addition of sodium bromide (1 mg/l Br⁻)
- addition of 5 mg/l of amidosulphonic acid.

After storage, the chlorine content in the samples was analysed (DPD method of Palin)*:

No.	pH	Bromide content	Amidosulphonic acid content	Chlorine content after 24 h
1	7.0	0	0	0.9 mg/l
2	7.0	0	5 mg/l	2.4 mg/l
3	7.0	1 mg/l	0	0.8 mg/l
4	7.0	1 mg/l	5 mg/l	2.4 mg/l
5	8.5	0	0	0.8 mg/l
6	8.5	0	5 mg/l	2.1 mg/l
7	8.5	1 mg/l	0	0.3 mg/l
8	8.5	1 mg/l	5 mg/l	2.3 mg/l

* Reference: M. Zimmermann (Editor) Photometrische Metall- und Wasseranalyse [Photometric analysis of metals and water], Wissenschaftl. Verlagsgesellschaft, Stuttgart 1974, Method B-C 1/3, variant 2:

5 Determination of "total active chlorine", including chloramines

Comments on Example 1:

Under pH conditions which are frequently encountered in cooling waters, the reaction of polyaspartic acid (10 mg/l as sodium salt) with bleaching liquor (5 mg/l as chlorine) were studied.

During storage at room temperature, as experiments Nos. 1 and 5 show, the bleaching liquor was >80% reacted, both at pH 7 and at pH 8.5, after 24 h; only 0.9 mg/l (pH 7) to 0.8 mg/l (pH 8), in each case measured as chlorine, were recovered.

The addition of bromide additionally intensifies the breakdown, especially at pH 8.5. [Bromide is oxidized under the experimental conditions present in this application from bleaching liquor to hypobromous acid whose biocidal action, especially at pH 8.5, is considerably stronger than that of the bleaching liquor.]

By adding amidosulphonic acid (Experiment Nos. 2, 4, 6, 8), under otherwise identical conditions, the reaction between polyaspartic acid and bleaching liquor (or, with addition of bromide, Experiment Nos. 4 and 8, in the additional presence of hypobromous acid) was considerably decreased: the residual contents of oxidizing agent are higher by a factor of 2.67 (comparison of Experiment Nos. 1 and 2) to 7.67 (comparison of Experiments 7 and 8).

Since the chemical reaction of chlorine with PAA, whose progress was measured in this application by the consumption of oxidizing agent, not only destroys the biocide, but presumably also the polymer, the degradation reaction is doubly harmful: the biocide added to protect the polymer from biodegradation is lost and can no longer

protect the polymer and the polymer itself can no longer develop its desired activity (corrosion protection and scale protection).

Example 2

5 (See Example 1 for experimental procedure)

Variant: Storage of the flasks at 60°C for 24 h

Results:

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No.	pH	Bromide content	Amidosulphonic acid content	Chlorine content after 24 h
1	7.0	0	0	approximately 0.1 mg/l
2	7.0	0	5 mg/l	1.9 mg/l
3	7.0	1 mg/l	0	approximately 0.1 mg/l
4	7.0	1 mg/l	5 mg/l	2.5 mg/l
5	8.5	0	0	approximately 0.1 mg/l
6	8.5	0	5 mg/l	1.2 mg/l
7	8.5	1 mg/l	0	approximately 0.1 mg/l
8	8.5	1 mg/l	5 mg/l	1.8 mg/l

Patent Claims

1. Composition for water treatment comprising

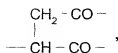
- 5 a) biodegradable organic polymers having repeating succinyl units
 b) a biocidal oxidizing agent
 c) an unsubstituted or substituted amidosulphonic acid.

2. Composition for water treatment according to Claim 1, characterized in that
 10 amidosulphonic acid of the formula

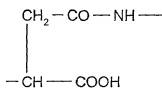
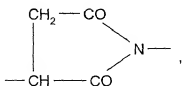


is used.

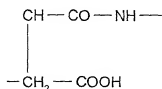
3. Composition for water treatment according to Claims 1 and 2, characterized
 15 in that the biodegradable organic polymers have repeating succinyl units of the structures



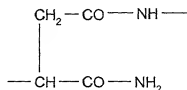
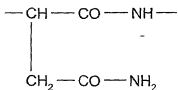
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β -form



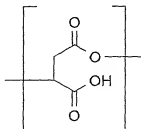
α -form



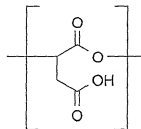
4. Composition for water treatment according to Claims 1 to 3, characterized in that the biodegradable organic polymers contain repeating units of the formulae

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- a) maleic acid units of the formula

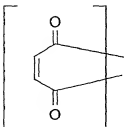


and

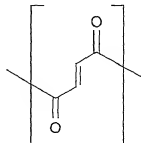


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- b) maleic acid and fumaric acid units of the formula



and



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5. Composition for water treatment according to Claims 1 to 4, characterized in that the biocidal oxidizing agent is hydrogen peroxide, chlorine, bromine, chlorine dioxide, hypochlorite, hypobromite, ozone or their reaction products with water.

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6. Use of the compositions according to Claim 1 for water conditioning in cooling circuits.

7. Process for water conditioning in cooling circuits, characterized in that compositions according to Claim 1 are used.

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Compositions for water treatment

A b s t r a c t

The present invention relates to compositions for water treatment based on biodegradable polymers containing repeating succinyl units, biocidal oxidizing agents and unsubstituted or substituted amidosulphonic acid, their use in, and the process for, conditioning water of cooling circuits.

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As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

MEDIA FOR WATER TREATMENT

the specification of which is attached hereto,

or was filed on **August 4, 1999**

as a PCT Application Serial No. **PCT/EP99/05640**

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s), the priority(ies) of which is/are to be claimed:

198 37 068.7
(Number)

Germany
(Country)

August 17, 1998
(Month/Day/Year Filed)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose the material information as defined in Title 37, Code of Federal Regulations, §1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)

(Filing Date)

(Status)

(patented, pending, abandoned)

(Application Serial No.)

(Filing Date)

(Status)

(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

JOSEPH C. GIL, Patent Office Registration Number 26,602
ARON PREIS, Patent Office Registration Number 29,426
LYNDANNE M. WHALEN, Patent Office Registration Number 29,457
THOMAS W. ROY, Patent Office Registration Number 29,582
RICHARD E. L. HENDERSON, Patent Office Registration Number 31,619
GODFRIED R. AKORLI, Patent Office Registration Number 28,779
N. DENISE BROWN, Patent Office Registration Number 36,097
NOLAND J. CHEUNG, Patent Office Registration Number 39,138
DIDERICO VAN EYL, Patent Office Registration Number 38,641
CAROLYN M. SLOANE, Patent Office Registration Number 44,339
JAMES R. FRANKS, Patent Office Registration Number 42,552
JACKIE ANN ZURCHER, Patent Office Registration Number 42,251

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all of Bayer Corporation, Pittsburgh, Pennsylvania 15205-9741

Send Correspondence To:

Patent Department

Bayer Corporation

100 Bayer Road

Pittsburgh, Pennsylvania 15205-9741

Direct Telephone Calls To:

(412) 777-2349

FULL NAME OF SOLE OR FIRST INVENTOR Roland Kleinstück		INVENTOR'S SIGNATURE <i>Roland Kleinstück</i>	DATE <i>2001-01-08</i>
RESIDENCE D 51467 Bergisch Gladbach, Germany		CITIZENSHIP German	
POST OFFICE ADDRESS c/o Bayer Aktiengesellschaft, D 51368 Leverkusen, Germany			
FULL NAME OF SECOND INVENTOR Torsten Groth		INVENTOR'S SIGNATURE <i>Torsten Groth</i>	DATE <i>2001-01-10</i>
RESIDENCE D 51519 Odenthal, Germany		CITIZENSHIP German	
POST OFFICE ADDRESS c/o Bayer Aktiengesellschaft, D 51368 Leverkusen, Germany			
FULL NAME OF THIRD INVENTOR Winfried Joentgen		INVENTOR'S SIGNATURE <i>Winfried Joentgen</i>	DATE <i>2001-01-12</i>
RESIDENCE D 50735 Köln, Germany		CITIZENSHIP German	
POST OFFICE ADDRESS c/o Bayer Aktiengesellschaft, D 51368 Leverkusen, Germany			
FULL NAME OF FOURTH INVENTOR		INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			
FULL NAME OF FIFTH INVENTOR		INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			
FULL NAME OF SIXTH INVENTOR		INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			
FULL NAME OF SEVENTH INVENTOR		INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			